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► To cite this version:

Arthur Valleron, Christophe Pijolat, Jean-Paul Viricelle, Philippe Breuil, Jean-Claude Marchand, et al.. Exhaust gas sensor based on tin dioxide for automotive application. 13th International Symposium on Olfaction and Electronic Nose ISOEN 2009, Apr 2009, Brescia, Italy. pp.450-451, 10.1063/1.3156578 . hal-00420392

HAL Id: hal-00420392

<https://hal.science/hal-00420392>

Submitted on 28 Sep 2009

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Exhaust Gas Sensor Based On Tin Dioxide For Automotive Application

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The aim of this paper is to investigate the potentialities of gas sensor based on semi-conductor for exhaust gas automotive application. The sensing element is a tin dioxide layer with gold electrodes. This gas sensor is able to detect both reducing and oxidizing gases in an exhaust pipe with varying selectivity depending on the temperature in the range 250°C-600°C. At low temperature 350-400°C, the sensor detects nitrogen dioxide while it is more sensitive to carbon monoxide at temperatures exceeding 500°C.

Keywords: Gas sensor, Tin Dioxide, Exhaust, Automotive.

PACS: 07.07.Df

INTRODUCTION

The new legislation obliges car manufacturers to reduce and control emissions. Hence, there are actually many researches on exhaust gas sensors. Most of them are based on devices issued from oxygen lambda sensors, mixed potential type sensors [1] using a solid electrolyte (often yttria stabilized zirconia, YSZ) as sensing element. On the contrary, there are few studies on this topic, using resistive gas sensors based on semi-conductor. This kind of gas sensor, in particular, tin dioxide sensors, is well known and is used in many areas such as, for example, process control, environmental control and domestic security [2]. So, in this study, we developed a robust gas sensors based on tin dioxide, able to work in exhaust harsh conditions. Its performances are studied on a synthetic gas bench.

EXPERIMENTAL AND METHODS

Sensors are made by screen-printing on an alumina substrate, one side of the substrate being used for the sensing layer and the other for the heating resistance. The thickness of the tin dioxide layer is about 40µm.

The sensors are tested in a bench which is able to submit sensors to high gas temperature (250°C-450°C)

and high gas speed ($v=5,6\text{m/s}$), with a gas flow of 80L/min. Two kinds of tests are performed.

Static Tests

In "static tests", the sensor temperature is increased step by step, and for each temperature, sensors are subjected to a carrier gas flow (12% O₂), then the target gas : CO in the range [50-1000ppm] and NO₂ in the range [50-350ppm]. The sensor's conductances in carrier gas flow (G₀) and in presence of pollutants (G) are measured. The sensitivity is represented by the relative response of the sensors : $(G-G_0)/G_0$ for reducing gases, and $(R-R_0/R_0)$ for oxidizing gases, with R₀ and R the sensing element resistances under carrier and target gas.

Dynamic Tests

These tests consist to study response time of sensors for responses to CO and NO₂. Sensors are successively subjected to a "base" gas and then mixed to the target gas at a certain frequency. For CO experiments, the "base" gas is constituted of O₂, H₂O, CO₂, NO and C₃H₈. 1000ppm of CO target gas is added periodically. For NO₂ experiments, "base" gas contains O₂, H₂O and CO₂, and NO₂ is injected as a target gas.

RESULTS AND DISCUSSION

Static Tests

The responses of the sensors to CO versus temperature are shown in Figure 1. The gas temperature was set at 250°C. The sensitivity to a fixed concentration continuously increases with varying rate versus the temperature.

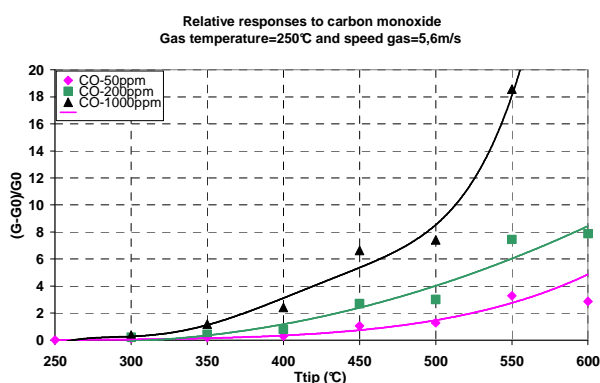


Figure 1. Relative response $(G-G_0)/G_0$ of the sensors to CO 50ppm, 200ppm and 1000ppm as a function of sensors temperature (Ttip).

The responses of the sensors to NO₂ are shown in Figure 2. Contrary to CO, the response curves versus temperature present a maximum of sensitivity. The responses are high in the range 300°C-500°C with a maximum at 350°C.

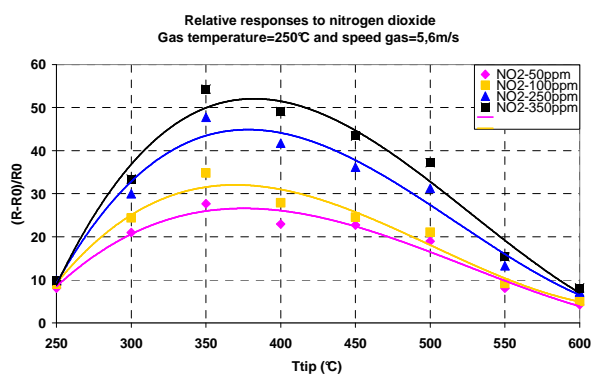


Figure 2. Relative response $(R-R_0)/R_0$ of the sensors to NO₂ 50ppm, 100ppm, 250ppm and 350ppm as a function of sensors temperature (Ttip).

As expected, we observe a reducing behaviour for CO and an oxidant one for NO₂.

The difference of behaviour is very interesting because it gives the opportunity to detect CO at high temperatures (550-600°C), while NO₂ can be detected at 350°C.

Dynamic Tests

CO responses in dynamic tests at 600°C are shown in Figure 3. Both response time and recovery time are approximatively one second. It is worthy to note, that even with the presence of NO and C₃H₈ in the “base” gas, we have a significant response to 1000ppm CO.

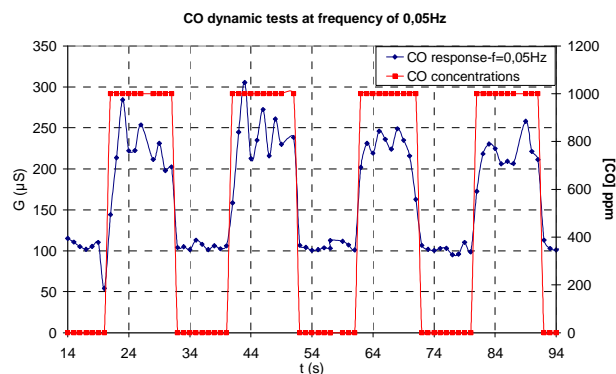


Figure 3. CO response in dynamic tests ($f=0,05\text{Hz}$).

For NO₂, (not shown here) response time is around 3 seconds but the recovery time is slower ($>15\text{s}$ at 300°C).

For automotive application, detection of CO at 600°C is possible, unlike NO₂ detection at 300°C, for which the recovery time may be too long. A solution could consist in a temperature pulse to recover the base signal.

CONCLUSIONS

Thus, SnO₂ sensors are able to detect CO at a temperature above 500°C on a first hand, and to detect nitrogen dioxide at a temperature below 400°C on a second hand. These performances can be used to make a device comprising two sensors based on tin dioxide and which is able to detect the two gases simultaneously [3]. Another solution is to use only one sensor but with temperature regulation for cycling monitoring of CO and NO₂ depending on the temperature.

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